

Behaviour of muonium in synthetic diamond

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1 Introduction

Diamond with its unsurpassed mechanical strength, thermal conductivity, and radiation hardness is a promising material for radiation detectors, for electronic and optical-electronic components able to withstand high heat and radiation loads. Great advances have been made over the last years in technology of manufacturing synthetic single-crystal diamond and diamond films [1, 2]. The properties of synthetic diamond should be comprehensively studied to find out the scope of its practical application.

Man-made bulk diamond samples (single crystals and films) contain about (or more than) 10^{17} cm^{-3} dissolved hydrogen atoms. Recently, surface conductivity was observed in a diamond sample saturated in a hydrogen atmosphere [3]. However, conventional methods do not yield sufficient information on the behaviour of hydrogen in diamond.

Polarized positive muons μ^+ can be used to imitate and study the behaviour of an hydrogen atom in matter (see, for example, [4, 5]). A positive muon in matter may pick up an electron and form muonium ($\text{Mu} = \mu^+e^-$). Since the muon mass is about 1/9 than that of the proton, muonium can be considered as a light isotope of hydrogen. Theoretical calculations [6, 7] show that in semiconductors with diamond crystal structure the muonium may occupy tetrahedral and octahedral interstitial sites or is localized in the middle of the axis between two host atoms (bond-centre site). It was experimentally found (see [8, 9]) that in diamond the muonium occupies the tetrahedral site (commonly referred to as normal muonium and designated as Mu or Mu_T) and the bond-centre site (commonly referred to as anomalous muonium and designated as Mu^* or Mu_BC). One more μSR signal corresponding to the diamagnetic state of μ^+ was observed in experiments (μ^+ -state).

In diamond Mu_T possesses isotropic symmetry with a hyperfine constant $A_\text{hf}/h = 3711 \pm 21 \text{ MHz}$ [8] ($A_\text{hf}/h = 3693 \pm 83 \text{ MHz}$ [10]), which is slightly smaller than that

for muonium in vacuum $A_0/h = 4463302.765 \pm 0.053$ kHz [11]. At the bond-centre site the hyperfine interaction is anisotropic with axial symmetry relative to the $[111]$ axes of the crystal. The hyperfine interaction constants of Mu_{BC} are $A_{\parallel}/h = 167.98 \pm 0.06$ MHz and $A_{\perp}/h = -392.59 \pm 0.06$ MHz [8]. For the muonium bond-centre site the muon spin precession frequency in a magnetic field depends on the angle between the magnetic field and the $[111]$ axes of the crystal. However, theoretical calculations [6, 7] reveal that for Mu_{BC} there is a certain ‘magic’ field where the muon spin precession frequency is nearly independent on the orientation of the crystal. This effect can be used to observe a Mu_{BC} signal at the ‘magic’ field in a powder sample.

The above-mentioned values of the hyperfine constants of the muonium were obtained for two natural diamond samples: Ia-type single-crystal diamond and IIa-type diamond powder with grain size 1–6 μm . In the present work the behaviour of the positive muon in two synthetic diamonds is studied.

2 Measurements

The measurements were carried out at the GPS and Dolly spectrometers located in the $\pi\text{M}3.2$ and $\pi\text{E}1$ muon beams of the Paul Scherrer Institut (PSI, Switzerland). In the $\pi\text{M}3.2$ beam line the muons were transversely polarized — the angle between the muon spin and the muon momentum was $\sim 70^\circ$.

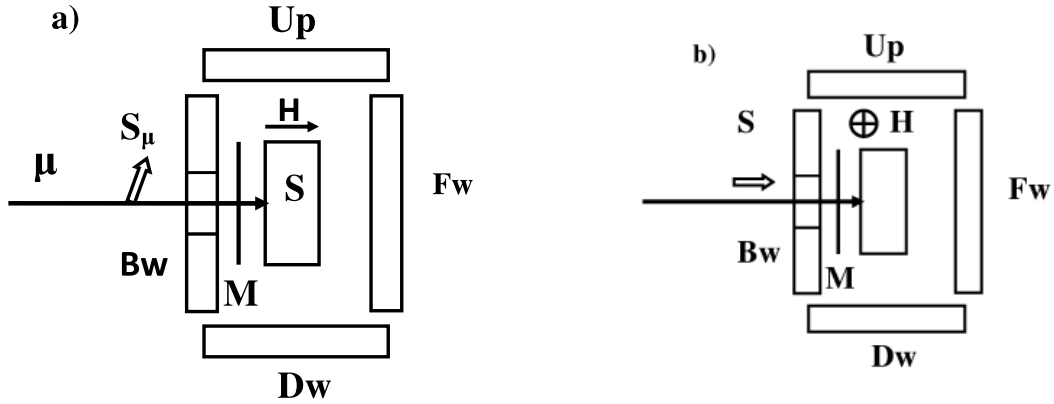


Figure 1: Location of the apparatus in the PSI muon beams. Up, Dw, Fw and Bw are the up, down, forward and backward telescopes for detection of positrons. M is the counter for registration of the incoming muons, H is the magnetic field, S is the sample, S_μ indicates the muon spin polarization direction. a) At the GPS spectrometer the muon beam is transversely polarized and the magnetic field is parallel to the incoming muon beam momentum. b) At the Dolly spectrometer the muon beam longitudinally polarized and the magnetic field is perpendicular to the picture plane.

The location of the apparatus in the PSI muon beams is schematically shown in Fig.1. Muons with energy ~ 4 MeV pass through the hole in the Bw counters and a thin M-counter and stop in the sample S. The positrons from the muon decay were detected by the Bw (backward), Fw (forward), Up(up) and Dw(down) telescopes located around the sample (see Fig. 1). A magnetic field transverse to the muon spin polarization at the sample was created by Helmholtz coils. The long-time stability of the magnetic field was better than 10^{-4} .

Measurements were carried out using a helium flow cryostat that allowed changing temperature of the sample within the range of 4.2–300 K. The temperature of the sample was stabilized with an accuracy better than 0.1 K. Measurements were carried out in ‘magic’ magnetic field $H_M = 0.4073$ T at the GPS spectrometer and in $H = 7.5$ mT at the Dolly spectrometer.

In these measurements two samples (designated as D3 and D5) were used. Sample D3 with the total mass of 2 g was composed of a few IIa-type single-crystal diamonds. Orientation of the crystals in the sample was random (MSC – mosaic single crystal). The concentration of nitrogen in sample D3 was about 0.5 ppm (in diamond, 1 ppm corresponds to $1.76 \cdot 10^{17} \text{ cm}^{-3}$). The crystals contain few wt% of Ni as isolated inclusions visible by eye. The diamond crystals with dimension 1–4 mm were synthesized at the Technological Institute for Superhard and Novel Carbon Materials (Troitsk, Russia) at high pressure and high temperature with synthetic diamond as seed material [12]. Sample D5 (CVD) of total mass 2 g was a batch of pieces of several diamond films 0.5 mm thick and about 10×5 mm in lateral size. The diamond films were produced by a microwave plasma assisted CVD technique in CH_4/H_2 mixtures [13]. The main impurities in sample D5 were hydrogen (65 ppm) and nitrogen (1.5 ppm). Other impurities were less than 0.1 ppm. The crystalline axis [110] perpendicular to the film plane was the predominant grain orientation.

The evolution of the muon polarization $P(t)$ was studied by measuring the time distribution of positrons from the decay of muons $\mu^+ \rightarrow e^+ + \nu_e + \bar{\nu}_\mu$. In the general case the time distribution of the positrons (with respect to muon stop in sample) can be presented by the function

$$N(t) = N_0 \exp(-t/\tau_\mu)(1 + \alpha/3 \cdot G(t)) + \text{Bg}, \quad (1)$$

where N_0 is proportional to the number of muons stopped in the sample, τ_μ is the muon lifetime, $G(t)$ is the polarization of the muon at the decay, α depends on the parameters of the μSR setup and is close to 1, Bg is background.

The function $G(t)$ depends on the experimental condition: for measurements at $H = 7.5$ mT and $H = 0.4073$ T the respective explicit expressions for $G(t)$ are

$$G(t) = P_\mu(0) \exp(-R_\mu t) \cos(2\pi\nu_\mu t + \varphi_0) + P_T(0) \exp(-R_T t) \cos(2\pi\Omega_1 t + \varphi_1) \cos(2\pi\Omega_2 t + \varphi_2), \quad (2)$$

$$G(t) = P_\mu(0) \exp(-R_\mu t) \cos(2\pi\nu_\mu t + \varphi_0) + P_{\text{BC}}(0) \exp(-R_{\text{BC}} t) \cos(2\pi\nu_M t + \varphi_1), \quad (3)$$

where $\Omega_1 = (\nu_{23} + \nu_{12})/2$; $\Omega_2 = (\nu_{23} - \nu_{12})/2$; ν_{ik} is the frequency of the transition between levels of hyperfine structure of Mu_T ; variables with indices μ , T and BC refer to the muon

in the diamagnetic, normal muonium and anomalous muonium states respectively; $P_i(0)$ is the muon polarization at $t = 0$; R_i is the relaxation rate of the muon spin; ν_M is the muon spin precession frequency for the Mu_{BC} fraction in the ‘magic’ magnetic field; φ_i is the initial phase of the muon spin precession.

3 Results and discussion

Figure 2 shows the results of Fourier transformation of the μSR spectra for sample D5 measured in the magnetic field 7.5 mT at the temperatures 50 and 250 K. The peaks at ~ 100.4 and ~ 105.8 MHz correspond to the transitions between the levels of the hyperfine structure of the muonium Mu_{T} . The narrowing of the lines ν_{12} and ν_{23} with increasing temperature was observed for both samples D3 and D5.

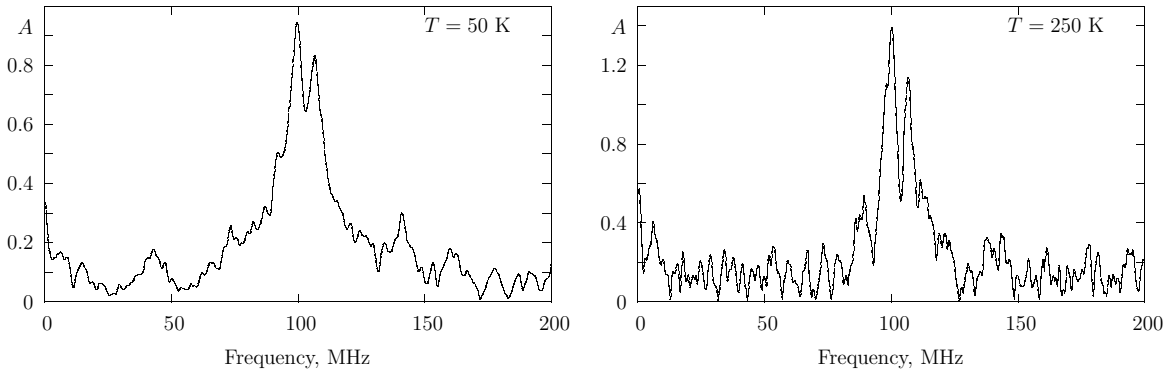


Figure 2: The result of the Fourier analysis of the μSR histograms for diamond film D5 measured in 7.5 mT magnetic field at the temperatures a) 50 and b) 250 K.

sample	50 K	100 K	200 K	250 K
D3 (MSC)	19.1 ± 0.8			13.4 ± 0.9
D5 (CVD)	12.4 ± 0.6	17.3 ± 1.4	12.3 ± 0.6	7.7 ± 0.6

Table 1: Muon spin relaxation rate R_T (MHz) for the Mu_{T} fraction in synthetic diamond at different temperatures.

The μSR spectra measured in the magnetic field 7.5 mT were fitted by (1) with polarization function (2) and values of the parameters $P_\mu(0)$, $P_{\text{T}}(0)$, R_{T} , ν_μ , Ω_1 and Ω_2 were found (see Table 1 and Table 2). It was found that R_μ is equal to zero, and final values for other parameters were obtained by fitting the experimental data with fixed $R_\mu = 0$. The values Ω_1 and Ω_2 presented in Table 2 correspond to more precise results

obtained at 250 K. Hyperfine constants were calculated as

$$A_{\text{hf}} = \frac{1}{2} \left[\frac{(\nu_{23} + \nu_{12} + \nu_{\mu})^2}{\nu_{23} - \nu_{12}} - (\nu_{23} - \nu_{12}) \right] = \left[\frac{(\Omega_1 + \nu_{\mu}/2)^2}{\Omega_2} - \Omega_2 \right]. \quad (4)$$

sample	ν_{μ} , MHz	Ω_1 , MHz	Ω_2 , MHz	A_{hf} , MHz
D3 (MSC)	0.996 ± 0.005	103.73 ± 0.12	2.95 ± 0.22	3715 ± 277
D5 (CVD)	0.992 ± 0.004	103.13 ± 0.06	2.75 ± 0.10	3940 ± 143

Table 2: Muon spin precession frequency and hyperfine interaction constant A_{hf} for Mu_T .

The values of the hyperfine constant for Mu_T in samples D3 and D5 are smaller than for muonium in vacuum, and they are in agreement with the value $A_{\text{hf}} = 3711 \pm 21$ MHz for natural diamond powder [8] within the accuracy of the measurements. However, a significant difference was observed in the behaviour of muonium in synthetic diamond in comparison with IIa-type natural powdered diamond [8]: 1) the muon spin relaxation rate R_T for samples D3 and D5 is approximately ten times higher than for the natural sample; 2) in distinction to results [8], Mu_T was observed at temperatures higher than 150 K, and at 250 K the relaxation rate decreases slightly (see also Fig. 2). At the same time the present results for the relaxation rate in synthetic samples D3 and D5 are close to those observed in [14] for IIa- and IIb-type natural diamonds.

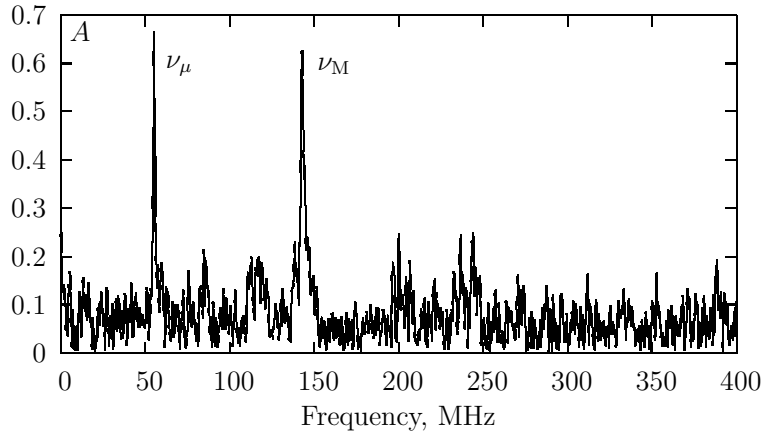


Figure 3: Muon spin precession frequencies observed in synthetic diamond D3 in the ‘magic’ magnetic field 0.4073 T at 100 K.

Figure 3 shows the results of the Fourier analysis of the μSR -data measured by the Up telescope of the GPS spectrometer for mosaic single crystal diamond sample D3 in the ‘magic’ magnetic field 0.4073 T at 100 K. There are two peaks: one corresponds to the precession of the muon spin in the diamagnetic state and the other is due to the

precession of the muon spin in the anomalous muonium in the ‘magic’ magnetic field. Muon spin precession frequencies of Mu_T too high to be observed in the “magic” field. The μSR histograms collected by the Up and Dw telescopes were fitted with polarization function (3) and values of the parameters R_{BC} , ν_μ and ν_M were extracted: $R_{\text{BC}} = 2.1 \pm 0.5$ MHz, $\nu_\mu = 55.224 \pm 0.005$ MHz and $\nu_M = 142.8 \pm 0.1$ MHz. As for the normal muonium in synthetic diamond D3, the relaxation rate of the muon spin in anomalous muonium is an order of magnitude higher than that observed earlier in IIa-type natural powder diamond (0.25 ± 0.10 [8]).

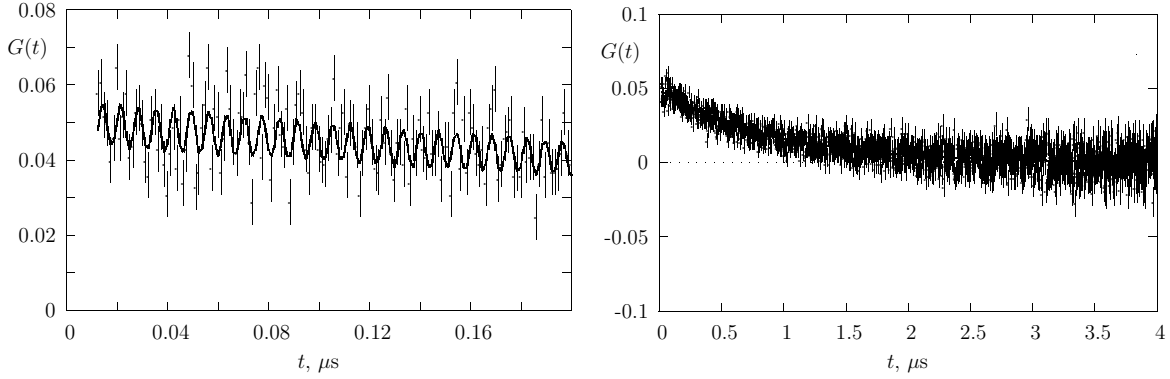


Figure 4: The time dependence of the muon polarization in diamond D3 in the magnetic field 0.4073 T for the case of longitudinal field measurements (LF). The data are corrected for the muon life time $\tau_\mu = 2197$ ns.

Since in the $\pi\text{M}3.2$ beam line the angle between the muon spin and the muon momentum is $\sim 70^\circ$ and the external magnetic field is parallel to the muon momentum, the μSR -histograms collected by the Fw and Bw telescopes (see Fig. 1a) contain information about evolution of the longitudinal (with respect to the magnetic field) component of muon polarization (LF measurement). In Fig. 4 the μSR histogram for sample D3 (MSC) collected by the Fw telescope at the magnetic field $H = 0.4073$ T and $T = 100$ K are presented on two different time scales. There are two components of muon polarization in the histogram: oscillating and non-oscillating. The Fourier analysis reveals only one frequency in the Fw and Bw μSR histograms which corresponds to muon spin precession of Mu_{BC} in the ‘magic’ magnetic field. It is evident that the oscillating component of polarization is due to the Mu_{BC} fraction. At the same time both Mu_T and Mu_{BC} fractions may contribute to the non-oscillating component of the Fw and Bw μSR histograms. These histograms were fitted by the polarization function

$$G(t) = P(0) \exp(-t/T_1) + P_{\text{BC}}(0) \exp(-t/T_1^{\text{BC}}) \cos(2\pi\nu_M t + \varphi), \quad (5)$$

where T_1 and T_1^{BC} are the longitudinal relaxation times for the non-oscillating and oscillating components of muon spin polarization.

The following values of the muon spin polarization parameters were found: $1/T_1 = 1.07 \pm 0.02$ MHz, $1/T_1^{\text{BC}} = 1.14 \pm 0.14$ MHz, $\nu_M = 142.68 \pm 0.06$ MHz. As was expected,

sample		T , K	μ^+ (%)	Mu_T (%)	Mu_{BC} (%)	MF (%)	Ref
powder IIa	n	4.2–90	< 10	18.5(0.9)	9.9(0.7)	> 60	[8]
powder IIa	n	296	< 5	-	14.5(1.3)	> 80	[8]
SC Ia	n	4.2	< 10	20(4)	11.9(0.9)	> 60	[8]
SC Ia	n	5–270	4(1)	0	-	-	[15]
SC IIa	n	300	8.1(3.0)	68.9(1.0)	22.7(0.8)	0.3(3.3)	[9]
SC IIa	n	5–300	6(1)	61(4)	26(3)	7(8)	[14, 15]
SC IIb	n	5–300	14(4)	53(4)	26(3)	7(6)*	[14, 15]
CVD	s	10–300	$\simeq 6$	$\simeq 50$	$\simeq 10^*$	$\simeq 34^*$	[15]
CVD	s	4.5	19.4	50.2	6.8	23.6	[16]
SC IIa	s	5	4	54	30	12	[18]
CVD	s	50–250	0.8(0.1)	60(1)	-	-	**
MSC IIa	s	100	1.5(0.1)	57(4)	8.1(0.4)	33.4(5)	**

Table 3: Fractions of muon states (μ^+ , Mu_T , Mu_{BC}) and missing fraction (MF) observed in samples of natural (n) and synthetic (s) diamonds. SC is single crystal diamond, and MSC is a sample composed from few single-crystal, CVD is chemical vapor deposited diamond film. *-we estimated according to the data presented in original publication. **-present data.

the value of the ν_M obtained from LF measurements is in good agreement with the results of the TF measurements (data collected by the Up and Dw telescopes).

To find the fraction of muon formation in the μ , Mu_T and Mu_{BC} states in diamond the values obtained for $\alpha \cdot P_\mu(0)$, $\alpha \cdot P_T(0)$ and $\alpha \cdot P_{BC}(0)$ were normalized to the muon polarization for the silver sample measured under the corresponding experimental condition. It was found that for the Up, Dw and Fw telescopes of the Dolly spectrometer $\alpha \cdot P_{Ag}(0)/3 = 0.270 \pm 0.001$ and for the Up and Dw telescopes of the GPS spectrometer $\alpha \cdot P_{Ag}(0)/3 = 0.240 \pm 0.001$. In the calculation it was taken into account that in the transverse magnetic field only 0.5 of the muon polarization in Mu_T and in ‘magic’ magnetic field 11/30 of the muon polarization in Mu_{BC} [8] gives experimentally observable precession signal. The fractions of muons formed in the μ^+ , Mu_T and Mu_{BC} states in diamond samples D3 and D5 are presented in Table 3 in comparison with the analogous data for various diamond samples studied earlier.

The data in Table 3 are divided into the three sets. The first set includes data for the Ia-type single-crystal and IIa-type powdered natural diamonds, the second set presents data for the IIa-type and IIb-type single-crystal natural diamonds and the third set is for the synthetic diamond. The Mu_T fraction is minimal and the missing fraction is maximal for the first set of samples. For the second set of samples the missing fraction of muon polarization is close to zero. In the synthetic samples the Mu_{BC} fraction is 2–3 times smaller than in the IIa- and IIb-type single-crystal natural diamonds. The large missing fraction in the IIa-type powder sample (with grain size 1–6 μm) was explained by diffusion of the Mu_T to the crystalline boundaries [7].

It was experimentally shown that a large missing fraction of the muon polarization in the Ia-type diamond is due to one more muonium state in the nitrogen-rich diamond [16, 17]. As is well known, Ia-type diamonds contain about 0.1% (1000 ppm) nitrogen impurities and they are aggregated to large defects forming A- and B-centres. At A-centres two nitrogen atoms occupied two nearest substitution sites. The calculation given in [17] shows that the muonium may occupy the bond centre site between the neighboring nitrogen atoms in the case of A-type defects and the site between the nitrogen molecules in the case of the B-type defects.

The concentration of nitrogen atoms in the IIa- and IIb-type natural diamond is approximately three orders of magnitude lower than in Ia-type diamond. The fact that the missing fraction of muon polarization in the IIa- and IIb-type natural diamond is close to zero indicates that nitrogen does not play any noticeable role in formation of muonium fractions in these samples.

In the synthetic diamond the concentration of nitrogen is close to that in the IIb- and IIa-type natural diamond. Therefore it is reasonable to compare the results for the samples studied in this work with those for IIa- and IIb-type natural diamond. As is seen from Table 3, in the synthetic samples the Mu_T fraction is comparable, the Mu_{BC} fraction is 2–3 times smaller and the missing fraction is a few times larger than in the IIa- and IIb-type single-crystal diamonds. The fact that the missing fraction in the synthetic diamond is 2–3 times smaller than in the nitrogen-rich Ia-type natural sample and 2–3 times larger than in the IIa- and IIb-type samples indicates presence of some other defects in the synthetic diamond in comparison with the natural one. The observed difference may be due to the high concentration (more than 10 ppm) of incorporated hydrogen and due to a small crystalline size (a large effective surface) in the CVD films and due to the presence of Ni inclusions in sample D3 (MSC).

4 Summary

It is found that the hyperfine constant for interaction of the muon and the electron magnetic moments on Mu_T and Mu_{BC} in the synthetic diamond is close to those in the natural diamond. The longitudinal relaxation rate of the muon spin in the Mu_{BC} state is measured for the first time: $1/T_1^{BC} = 1.07 \pm 0.02$ MHz. The Mu_T fraction of the muon polarization and the relaxation rate R_T for the synthetic samples are comparable with those for the IIa- and IIb-type natural diamond.

The fact that 1) the missing fraction of the muon polarization in the synthetic samples is 2–3 times smaller than in the Ia-type natural sample and 2) the Mu_T fraction and the relaxation rate R_T for the synthetic samples is comparable with those for the IIa- and IIb-type natural diamond indicates to the low concentration of such defects as A- and B-centers in synthetic samples.

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